A Measurement of Lifetimes of Excited

States of Ionized Nitrogen Atoms

by

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APPROVAL BY THESIS DIRECTOR

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ACKNOWLEDGMENTS

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ABSTRACT

A beam of diatomic nitrogen ions, transmitted through a thin carbon foil, produced optical spectra of singly and doubly ionized nitrogen atoms as a result of collisions in the foil. Photographs of the resolved spectrum of this ionized nitrogen beam were examined. Since the beam particles were monoenergetic, an analysis of the decay in intensity of the individual spectral lines yielded the mean lifetimes of the emitting energy levels. The measurement of this variation in intensity along a spectral line was accomplished by microphotometric techniques. It was found that some of the excited states of singly and doubly ionized nitrogen have mean lifetimes of the order of 10^{-8} seconds.

Author

1. INTRODUCTION

The experimental determination of atomic parameters has for the most part been accomplished by a spectral analysis of thermal light sources. These sources include flames, arcs, sparks, ovens, hot-cathode diodes, and shock tube apparatus. Two major types of thermal light sources have emerged. These are the well-stabilized arc and the shock tube, both of which have distinct advantages. The well-stabilized arc permits precise and detailed intensity measurements, while shock tubes permit the variation of the temperature and pressure so as to obtain optimum conditions for the measurement of a given spectral parameter.

One of the atomic parameters which may be measured in the laboratory is the absorption oscillator strength of a particular atomic transition. Once the light from the element in question has been spectrally analyzed, the relative oscillator strength of a transition may be calculated from the relative intensity ratios of the spectral lines, which correspond to individual transitions. The relationship used to calculate these line oscillator strengths when a plasma is the light source is derived by Griem (1964) with

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the assumption of local thermodynamic equilibrium. This relationship between the line intensities and oscillator strengths, which is valid for transitions in different ionization stages, is

$$\frac{I'}{I} = \frac{f'g'}{f\,g} \left(\frac{\lambda}{\lambda'}\right)^3 (4\pi^{3/2}\, a_0^3 N_e)^{-1} \left(\frac{kT}{E_H}\right)^{3/2} \exp\left[-\frac{E' + E_\infty - E - \Delta E_\infty}{kT}\right] \quad (1)$$

where I represents the measured intensity of the spectral line, N_e is the electron density in the plasma source, a_0 is the Bohr radius, ΔE_∞ is the reduction of the ionization energy E_∞ of the lower ionization state which is due to the Coulomb interaction in the plasma, E_H is the ionization energy of hydrogen, g is the statistical weight of the lower level of the transition, f is the absorption oscillator strength, λ is the wavelength, T is the absolute temperature, and the other symbols are universal constants. In equation 1, the primed quantities refer to the transition in the higher ionization stage. Unless the absolute oscillator strength and intensity of a well-known standard transition are known, equation 1 enables only the evaluation of relative absorption oscillator strengths.

The determination of absorption oscillator strengths by equation 1 presents several difficulties inherent in the light sources themselves. For example, in order to obtain accurate results, it is essential to know the temperature and the electron density of the plasma source precisely. In addition, particular types of sources introduce further complications. However, the main disadvantage of thermal light sources is their inherent inability to produce highly ionized atoms. Thus the experimental determination of oscillator strengths through the use of thermal light sources is limited primarily to transitions in neutral and singly ionized atoms.

In general, for a spontaneous transition from an upper energy level u to a lower energy level l, the change in population of level u per unit time is given by

$$\frac{dN}{dt} = \sum_l A_{ul} N,$$ (2)

where A_{ul} is the Einstein coefficient for the transition between state u and state l and N is the instantaneous population of state u. Thus the transition probability per unit time from state u becomes

$$A_u = \sum_l A_{ul}$$ (3)

where the summation is over all possible lower states. The
mean lifetime of state u is defined as

$$\tau_u = \frac{1}{A_u} \qquad (4)$$

The $A_{u\ell}$ may be evaluated from equations 3 and 4 if
the relative initial intensities of all possible transitions
from state u are known. The relationship between the in-
tensity of a transition and the $A_{u\ell}$ is

$$I_{u\ell} = A_{u\ell} \, h \, \nu_{u\ell} \, N_u \qquad (5)$$

where $I_{u\ell}$ is the intensity of the transition from state u
to state 1, $\nu_{u\ell}$ is the frequency of the emitted photons, h
is Planck's constant, and N_u is the population of state u.
Once the $A_{u\ell}$ for a particular transition has been determined,
the absorption oscillator strength is given by

$$A_{u\ell} = \frac{2r_0 \omega^2 g_u}{g_\ell c} \, f_{\ell u} \qquad (6)$$

where g is the statistical weight of the level, $f_{\ell u}$ is the
absorption oscillator strength, ω is the angular frequency
of the emitted photons, r_0 is the classical electron radius,
and c is the speed of light in a vacuum.

Thus the determination of absorption oscillator
strengths by means of equation 6 is seen to be dependent on
knowing the mean lifetime of an excited state and the rela-
tive intensities of all possible transitions from that excited
state. Bashkin (1961) proposed the use of ion beam techniques
to produce emission spectra. These techniques appeared
(Bashkin, 1963) to alleviate many of the problems confronting
atomic spectroscopists in the experimental determination of
atomic parameters. The ion beam technique permits a direct
evaluation of the mean lifetime of an excited atomic state
and the relative intensities of all possible transitions
from the excited state.

The ion beam technique consists of passing a beam
of fast ions, generated by a Van de Graaff accelerator,
through a thin foil. In the foil, the beam particles are
further ionized and excited. The light from the decay of the
foil-excited ions to lower electronic states is analyzed by
means of a spectrograph, the entrance slit of the spectrograph
having been aligned parallel to the axis of the beam. Since
the beam is composed of one atomic species and is monoenergetic,
the velocity of the beam particles is constant and the dis-
tance along an individual spectral line may be converted
into a time scale. When the decay in intensity with distance

of a spectral line has been determined, the mean lifetime of
the upper state of the transition represented by the spectral
line may then be evaluated.

In 1964, Bashkin et al. obtained mean life data
using the ion beam technique. Light from beams of D, He,
C, N and O was analyzed by means of a grating spectro-
graph. It is the purpose of this thesis to discuss the
evaluation of mean lifetimes for some excited electronic
states of nitrogen in the visible region from the data
obtained in the above experiment.

Figure 1. Spectral lines from a fast nitrogen beam.

2. EXPERIMENTAL PROCEDURE

In the experiment performed by Bashkin et al. (1964), the ion beam technique was used as a light source. The incident beam, consisting of positively charged diatomic nitrogen ions, had an energy of 1.2 Mev before passing through a carbon foil. The Van de Graaff accelerator used to generate the nitrogen beams was furnished by the U. S. Naval Research Laboratory, Washington, D. C. The nitrogen beams were passed through carbon foils which were approximately 10 $\mu g/cm^2$ thick.

The light from the foil-excited nitrogen beam was analyzed with an f/0.8 grating spectrograph of the Naval Research Laboratory. The slit and grating rulings of the spectrograph were parallel to the axis of the nitrogen beam. The spectrograph had a dispersion of approximately 140 Å per mm and the magnification of the optical system at the photographic plate was 0.0369. Kodak 103a-f spectroscopic emulsions were used to record the transitions between 3500 Å and 6800 Å. Figure 1 shows a typical photographic plate obtained in the experiment. In figure 1 the beam current is 0.35 μamp., the plate exposure time is 18.9 minutes, and the incident beam energy is 1.2 Mev.

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Since photographic emulsions were used to record the de
decay in intensity of individual spectral lines as a function
of time, several factors must be considered in order to
determine accurate relative intensity ratios, which are used
to calculate mean lifetimes. First, it is necessary to
relate the plate blackening to the intensity of the light
producing the blackening; second, the plate density responds
nonlinearly to different intensities and the sensitivity of
the plate varies nonlinearly with wavelength; third, the
characteristics of the unexposed plate change with age and
storage conditions and the characteristics of the exposed
plate depend on the length of time between exposure and
development; and finally, the density of the developed image
is related to the type of developer used, development time,
temperature of the developer, concentration of developer, and
the type of agitation used in the development process (Mees,
1954).

Another consideration involves the characteristic
curve, which contains the results of the photographic cali-
bration procedure. The characteristic curve is a plot of
per cent transmission of the photographic plate vs. exposure.
Exposure is defined as the time integral of the intensity of
the light illuminating the photographic plate. In general
there are two types of characteristic curves, time scale and

intensity scale. Time scale implies that the exposure was varied by changing the exposure time while maintaining the intensity of the illuminating source at a constant value. Intensity scale implies that the exposure is varied by maintaining the exposure time at a constant value while changing the intensity of the illuminating light. However, if the photographic calibration procedure is constant and the range of densities is the same, the time scale characteristic curve is not the same as the intensity scale characteristic curve. This is a consequence of the reciprocity law failure. Thus if the intensity data are recorded in a situation where the exposure time is held constant, the calibration of the photographic plate must be made by use of an intensity scale characteristic curve.

In order to obtain accurate intensity measurements, the density ranges of the calibration plates have to correspond to the density of the spectral lines to be analyzed. Thus the characteristic curve should be well defined in the region where the densities of the spectral lines occur. These problems are solved by using a calibration source of approximately the same intensity as the source of emission lines and passing the light from the sources, emission and calibration, through the same optical system.

The development problems can be resolved by rigidly controlling the temperature and concentration of the developer, the development time, and the agitation procedure. For example, mechanical agitation is not adequate to minimize the Eberhard effect. For complete development, the photographic plate should be brushed several times per second with a camel's hair brush during development.

To correct for the reciprocity law failure and the frequency dependence of the photographic film response, it is necessary to plot a characteristic curve for each spectral line to be analyzed. The data for these curves were obtained by exposing different photographic plates (Kodak 103a-f) to a National Bureau of Standards calibrated light bulb of temperature 2854°K. The exposure times ranged from 2 seconds to 64 seconds while the intensity of the illuminating light bulb was maintained at a constant value. Figure 2 shows a typical curve obtained from these data.

Thus it is seen that in evaluating intensities of spectral lines through the use of photographic techniques, the photographic calibration procedure is a critical factor. In the experiment from which the data used in this thesis were obtained, the actual development techniques were
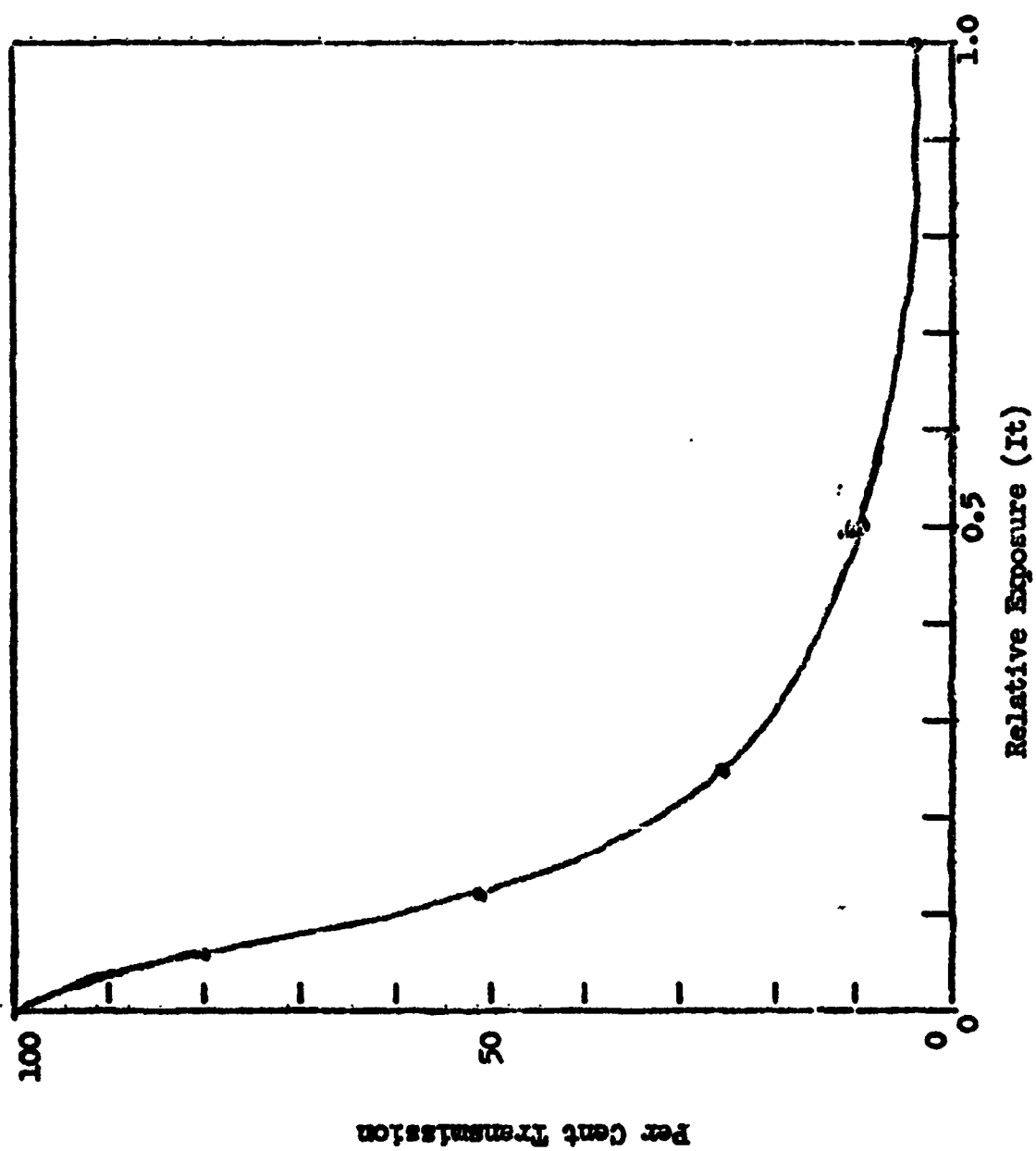
Figure 2. Characteristic curve for λ = 4867.2 Å.

standardized. However, systematic error was introduced into the mean life calculations through improper corrections for the reciprocity law failure.

There were two main contributing factors to this systematic error. First, since the intensity data were taken at constant exposure times, intensity scale characteristic curves should have been used in the calibration procedure instead of time scale characteristic curves. Second, the calibration light source was not approximately of the same intensity as the beam. Thus, due to the reciprocity law failure, evaluations of absolute and relative line intensities were somewhat in error.

3. MEAN LIFETIME DETERMINATION

The analysis of the photographic plates containing the emission spectra of the excited nitrogen beam was directed towards obtaining the decay in intensity as a function of the distance along each line. Since the decrease in density of developed film along a spectral line is a measure of the decay in intensity along the line, the Steward Observatory Hilger-Watts recording microphotometer was used in the analysis of the photographic plates to determine this decay in intensity along each individual spectral line.

At the plate, the microphotometer analyzing beam had a rectangular cross-sectional area whose dimensions could be changed by means of an adjustable slit. The photographic plate was oriented with respect to the analyzing beam so that the slit width was perpendicular to the line to be examined (figure 3). The decrease in density of the developed photographic plate along the line was obtained by traversing the spectral line in a direction parallel to the line. The slit length was adjusted to the widest portion of the spectral line while the slit width was set at a constant 0.036μ at the plate during the scanning procedure. Since the micro-
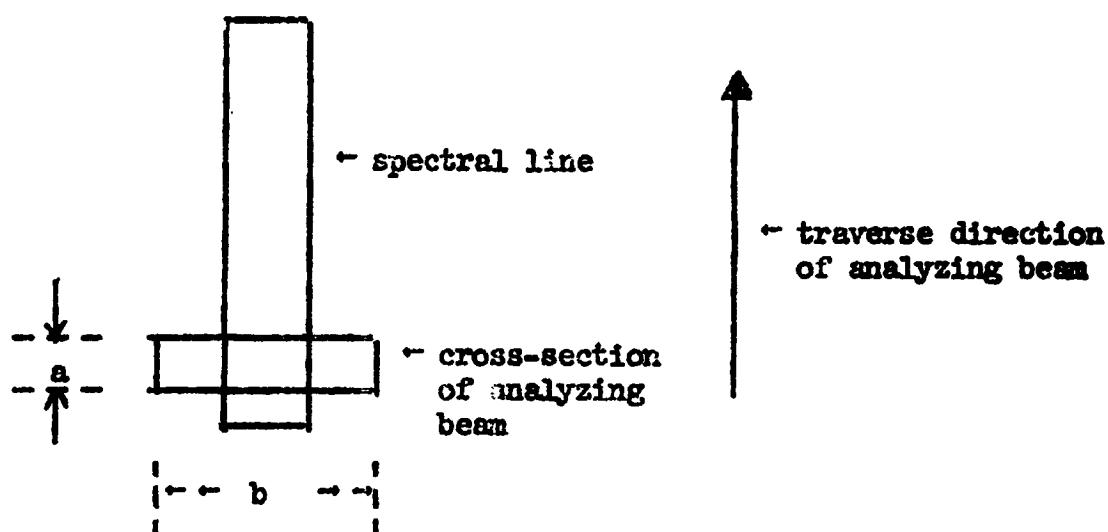
Figure 3. Position of cross sectional area of photometer beam with respect to spectral line.

Dimension a is controlled by the slit width adjustment while dimension b is controlled by the slit length adjustment.

photometer actually records per cent transmission, a decrease in per cent transmission was obtained as a function of distance along the spectral line. The microphotometer was initially set to record 100% transmission on the unexposed sections of the photographic plate. The lines selected for measurement from a photographic plate had at least a 50% transmission at the base of the line. This criterion enabled the determination of mean lifetimes with a minimum of interference from noise effects on the plate.

Using the characteristic curve for a particular spec-
tral line and the microphotometer tracing of that line, which
gives the transmission of the developed plate as a function
of the distance, it was possible to determine the actual
intensity decay as a function of distance along the line.
Figure 4 shows the intensity decay along the line as a function
of time plotted in a semi-log form using the calibration data
contained in the characteristic curve of Figure 2. Similar
intensity decay curves for the remaining spectral lines that
were analyzed appear in appendix A.

In the experiment, each diatomic nitrogen ion possessed
an energy of 1.2 Mev before passing through the 10 $\mu g/cm^2$ carbon
foil. Since the stopping power of nitrogen ions in carbon is
approximately 0.1 $\dfrac{Kev}{\mu g/cm^2}$, the nitrogen ions lost about
1 Kev while traversing the carbon foil (Northcliffe, 1963).
By using the equation

$$v = \sqrt{\frac{2E}{m}} \tag{7}$$

and taking into account the energy loss in the foil, the
velocity of the nitrogen ions after passing through the
carbon foil was found to be 2.87 x 10^8 cm/sec. Using this
value for the velocity of the nitrogen ions, it is then

possible to convert the distance along the spectral line into a time scale, as is shown in Figure 4.

The mean lifetime, τ, of a transition is defined by the exponential equation

$$I = I_o \exp\left[-\frac{t}{\tau}\right] \qquad (8)$$

By solving equation 8 for τ, we have the relationship used to calculate the mean lifetime. This relationship is

$$\tau = \frac{-d}{v \ln(I/I_o)} \qquad (9)$$

where d is the distance traveled by the nitrogen ions during a period of time t. By using the information contained in Figure 4 and the curves in appendix A, the mean lives of some of the optical transitions for singly and doubly ionized nitrogen ions were obtained. The results of these calculations are displayed in table 1 and table 2. In table 3, f_c, refers to a value for the absorption oscillator strength calculated from the experimental value of the mean lifetime of the transition and f_t refers to a theoretical calculation of the absorption oscillator strength using the Coulomb approximation to the wave function (Griem, 19). It should be noted,
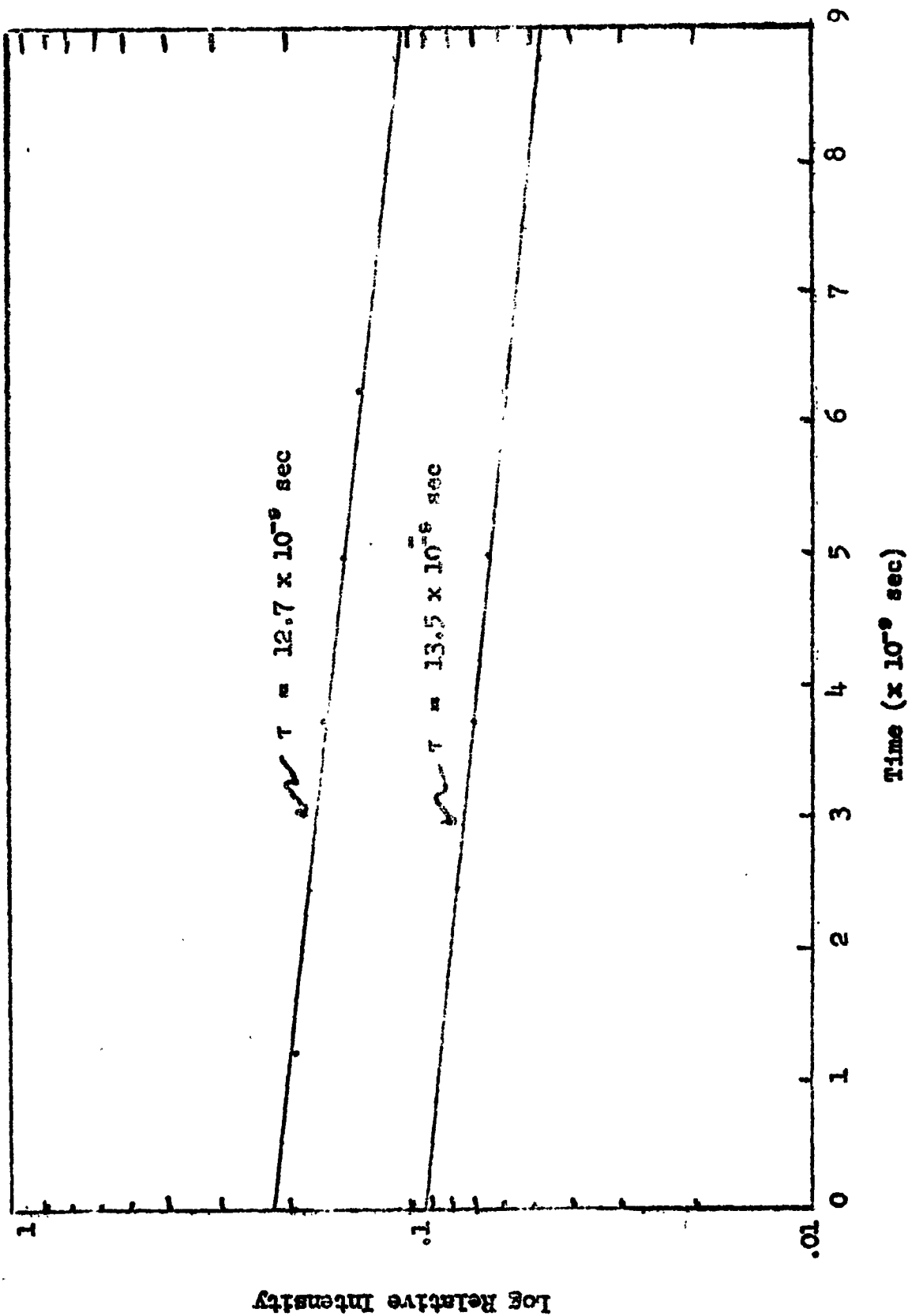
Figure 4. Intensity decay for N III, λ = 4867.2 λ
$2s2p(^3P^o)3p\,^4D_{3/2} - 2s2p(^3P^o)3d\,^4F^o_{5/2}$

however, that the reciprocal of the mean life was used for A_{ul} in equation 6. Thus, through consideration of equations 3, 4, and 6, it is seen that f_c represents an upper limit on the actual value of the absorption oscillator strength for a particular transition.

An iron comparison spectrum was used to determine the wavelengths of the nitrogen lines. In Figure 1, the iron lines are present at the base of the nitrogen lines. Due to the rather low dispersion of the spectrograph it was only possible to identify the nitrogen lines to within 2 angstroms. The presence of cascade effects (see chapter 4) in the transition schemes enabled the further identification of the nitrogen lines. The results of this identification procedure are presented in tables 1 and 2.

Table 1. Mean lifetimes of some excited states of N II.

$\lambda(\text{Å})$	Transition	Plate #	Mean Lifetime $\tau(\times 10^{-9}\text{ sec})$	$\bar{\tau}(\times 10^{-9}\text{ sec})$
5679.6(3)	$3s\ ^3P^o_2 - 3p\ ^3D_3$	105 107 107	19.6 24.0 24.0	21.8
5535.4(63)	$3s\ ^3P_3 - 3p\ ^3P^o_4$	105 107	13.7 11.8	12.7
5175.9(66)	$3p\ ^3D_3 - 3d\ ^3F^o_4$	105 105 107	2.05 2.61 3.11	2.59
5005.1(19)	$3p\ ^3D_3 - 3d\ ^3P^o_4$	105 106	14.5 16.3	15.4
4431.8(55) 4432.7(55) 4433.5(55)	$3d\ ^3P^o - 4p\ ^3D$	105	4.44	4.44
4041.3(39)	$3d\ ^3P^o_4 - 4f^2G_5$	105 109	6.35 6.96	6.66

Table 2. Mean Lifetimes of some excited states of N III.

λ(Å)	Transition	Mean Lifetime		
		Plate #	$\tau(\times 10^{-9} \text{sec})$	$\bar{\tau}(\times 10^{-9} \text{ sec})$
4867.2(9)	$3p\ ^4D_{7/2} - 3d\ ^4F^o_{9/2}$	105 106	12.7 13.5	13.1
4634.2(2)	$3p\ ^2P^o_{1/2} - 3d\ ^2D_{3/2}$	105 106 109	6.14 7.03 6.45	6.45
4535.1(13)	$3p\ ^4S_{3/2} - 3d\ ^4P^o_{5/2}$	105 109	13.5 12.7	13.1
4514.9(3)	$3s\ ^4P^o_{5/2} - 3p\ ^4D_{7/2}$	106 109 110	12.6 8.8 12.8	11.4

Table 3. Some absorption oscillator strengths for N II and
N III transitions.

λ(Å)	Charge State	f_c	f_t
5679.6	II	0.312	0.357
5535.4	II	0.467	0.336
5175.9	II	1.98	0.446
5005.1	II	0.314	0.557
4867.2	III	0.340	0.279
4634.2	III	0.985	0.428
4535.1	III	0.236	0.304
4514.9	III	0.328	0.286

4. CONCLUSION

Tables 1 and 2 list the results of the mean life analysis. Since the photographic calibration procedure is so critical in the determination of intensities from photographic emulsions, no attempt was made to assess an experimental error bound to the mean lifetimes listed in tables 1 and 2. The measured value of the mean life was used in equation 6 to calculate the upper limit, f_c, of the oscillator strengths for the transitions that were investigated. A theoretical value, f_t, of these absorption oscillator strengths is included in table 3 for comparison with the experimental calculations. Griem states that these theoretical values may vary as much as 20% from the true absorption oscillator strengths.

In 1965, Kay studied the identification of nitrogen lines obtained through the use of ion beam techniques. Although the experiment was not designed to evaluate mean lifetimes of excited states, three lifetimes were obtained. These lifetimes, τ_k , are listed in table 3 along with the corresponding lifetimes, τ_m , evaluated in this thesis. It

is seen that the results quoted by Kay agree to within a
factor of 30% to the results obtained in this thesis.

Another effect which introduces complications into
the mean life analysis is a cascade effect. Due to the
selection rules governing the transitions, the more ener-
getic excited states do not always decay directly to the

Table 3. Mean lifetimes of some excited states of nitrogen
as obtained by Kay (1965).

$\lambda(\text{Å})$	Charge State	$t_k(x\ 10^{-9}sec)$	$\tau_m(x\ 10^{-9}sec)$
5535(63)	II	9	12.7
4380(17)	III	4.5	
4514(3)	III	7	11.4

ground state. As the excited states with higher energy decay
into lower states, transition chains are established to the
ground state. If the transition is one which has no parent
level, i. e., a more energetic level that decays into the
upper level of the transition in question, then the analysis
is as described previously. However, in the presence of
a transition chain, the procedure is more involved. In
principle, the mean lives of the particular transitions
present in the transition chain may be determined by solving

the appropriate system of differential equations. The initial populations of the levels are an essential part of such an analysis and may be found through the use of equation 5.

The ten transitions listed in tables 1 and 2 yielded decay curves which were straight lines when plotted on semi-log paper. The fact that the decay curve was a straight line implies that one of three conditions was satisfied by the transition. First, the upper level of the observed transition had no parent transition; second, the mean life of the upper level of the parent transition was much smaller than the mean life of the upper level of the daughter transition; or third, the mean life of the upper level of the parent transition was much greater than the mean life of the upper level of the daughter transition. If the mean lives of the parent-daughter combination are of the same order or the number of parent transitions is more numerous than one, the situation becomes more complex. Many of the spectral lines that were analyzed yielded unfamiliar curves when plotted on semi-log paper. The latter results were attributed to the more complicated transition effects discussed above.

Griem (1964) reports that most of the experimental
values of the oscillator strengths, and therefore the mean
lifetimes, as previously determined, may well be in error
by a factor of 2 or 3. This error is mainly due to the use
of plasma light sources. It is also estimated that
eventually, as experimentation becomes more precise, a
system of oscillator strengths will evolve with an accuracy
approaching 10%. Although there isn't any previous experi-
mental data on multiply ionized atoms, the results obtained
in this thesis are seen to be in agreement with Kay's work
and in rough agreement with the theoretical values, without
proper photographic calibration procedure. McMurray (1961)
reports that if careful processing procedures are
rigorously standardized and followed for all photographic
plates, results reproducible to 2% are obtainable. Thus it
is seen that the ion beam technique coupled with the method
of analysis discussed in this thesis could be a very valuable
tool in the experimental determination of absorption oscillator
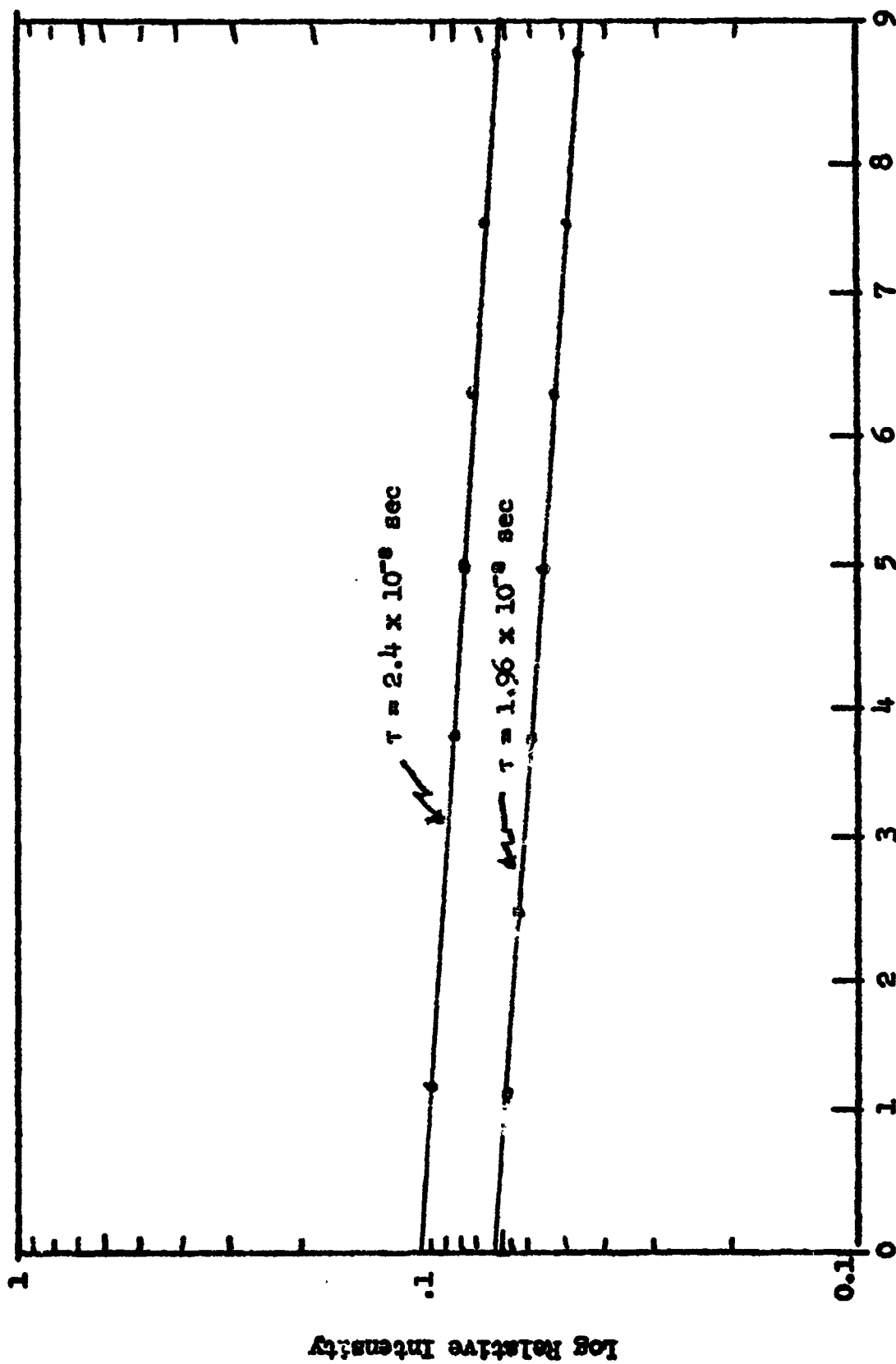strengths.

APPENDIX A

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Figure 5. Intensity decay for N II, λ = 5679.6 Å.

$2s^2 2p(^2P^o)3s \, ^3P^o_2 - 2s^2 2p(^2P^o)3p \, ^3D_3$

τ = 2.4 x 10⁻⁸ sec

τ = 1.96 x 10⁻⁸ sec
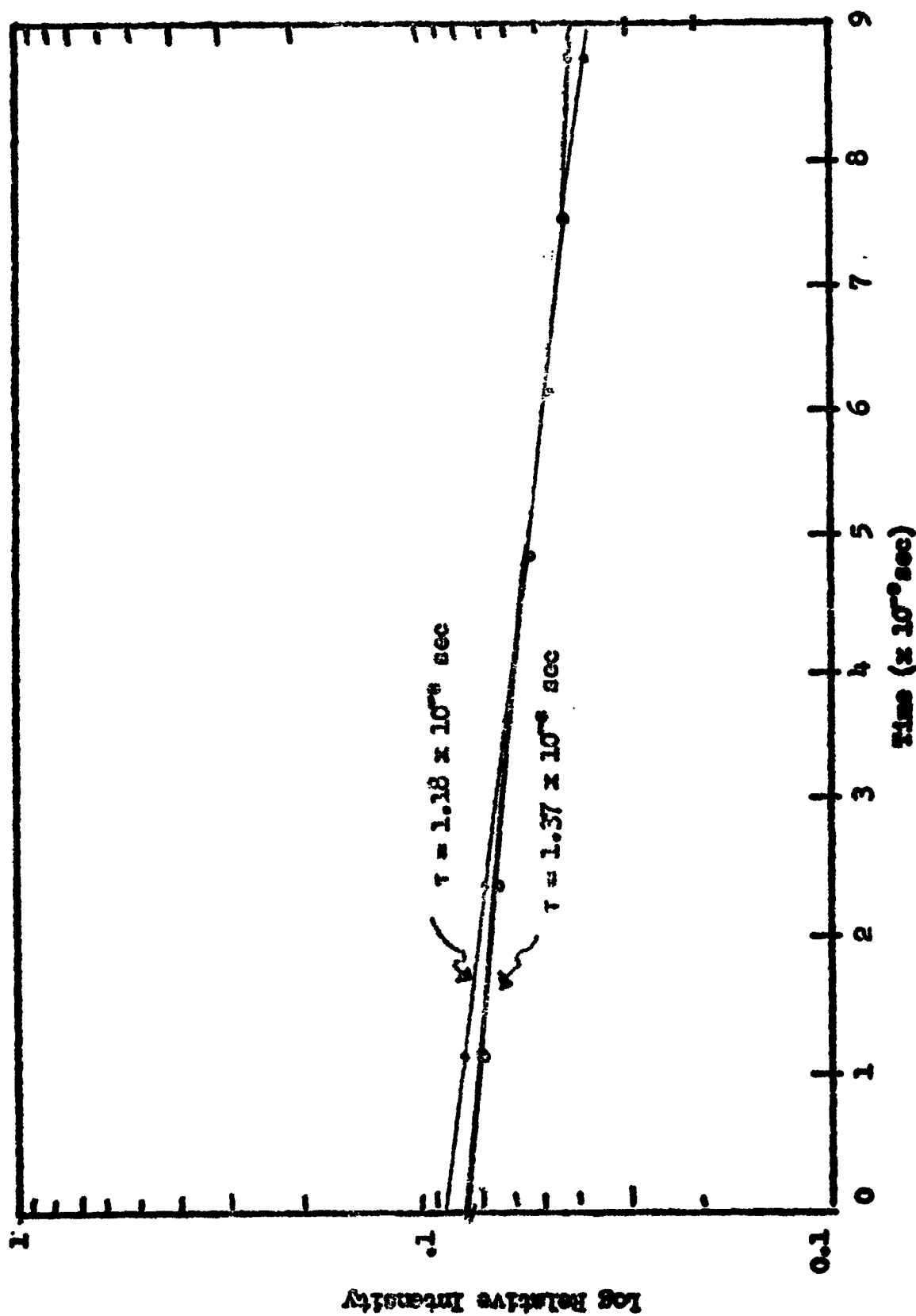
Figure 6. Intensity decay for N II, λ = 5535.4 Å.
2s2p²(⁴P) 3s⁴P - 2s2p²(⁴P) 3p⁴P
2s2p²(⁴P) 3p⁴P - 2s2p²(⁴P) 3d⁴F

τ = 1.18 x 10⁻⁸ sec

τ = 1.37 x 10⁻⁸ sec

Time (x 10⁻⁸ sec)

Log Relative Intensity
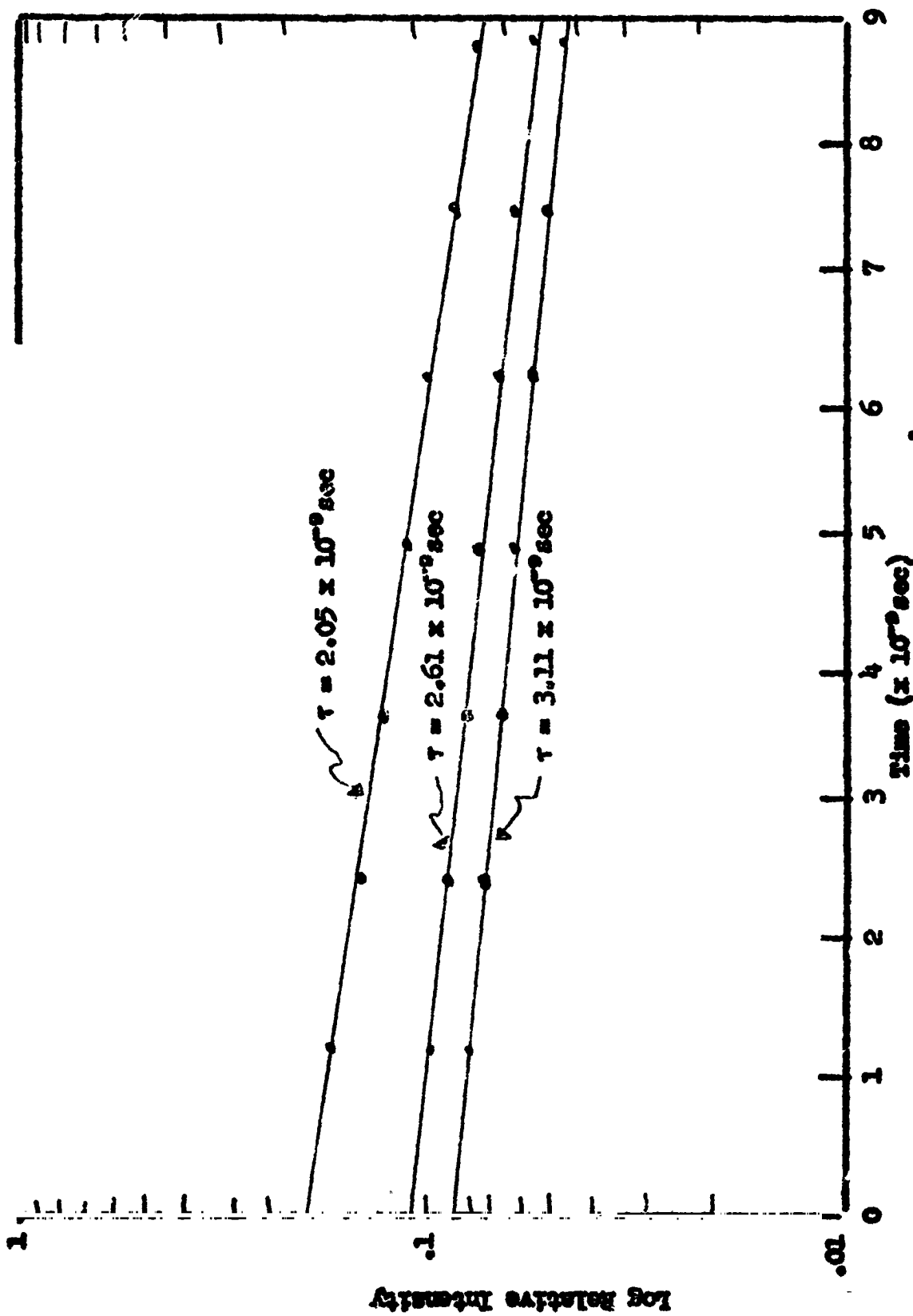
Figure 7. Intensity decay for I II, $\lambda = 5175.9$ Å.

$\tau = 2.05 \times 10^{-9}$ sec

$\tau = 2.61 \times 10^{-9}$ sec

$\tau = 3.11 \times 10^{-9}$ sec

Log Relative Intensity

Time (x 10^{-9} sec)
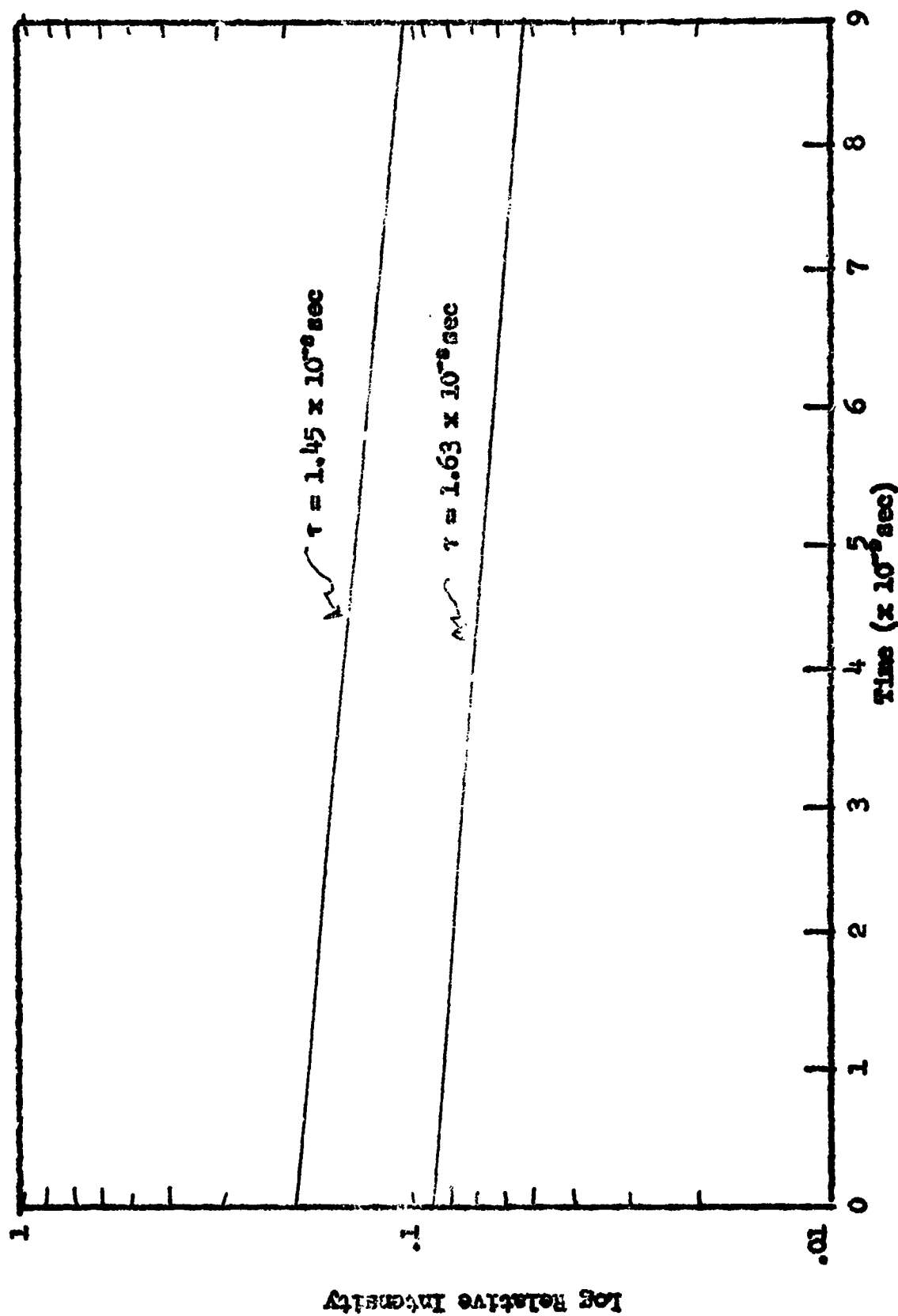
Figure 8. Intensity decay for N II, $\lambda = 5005.1$ Å.
$2s^2 2p(^2P^o)3p\,^3D_3 - 2s^2 2p(^2P^o)3d\,^3P^o_4$.

$\tau = 1.45 \times 10^{-8}$ sec

$\tau = 1.63 \times 10^{-8}$ sec

Time ($\times 10^{-5}$ sec)

Log Relative Intensity
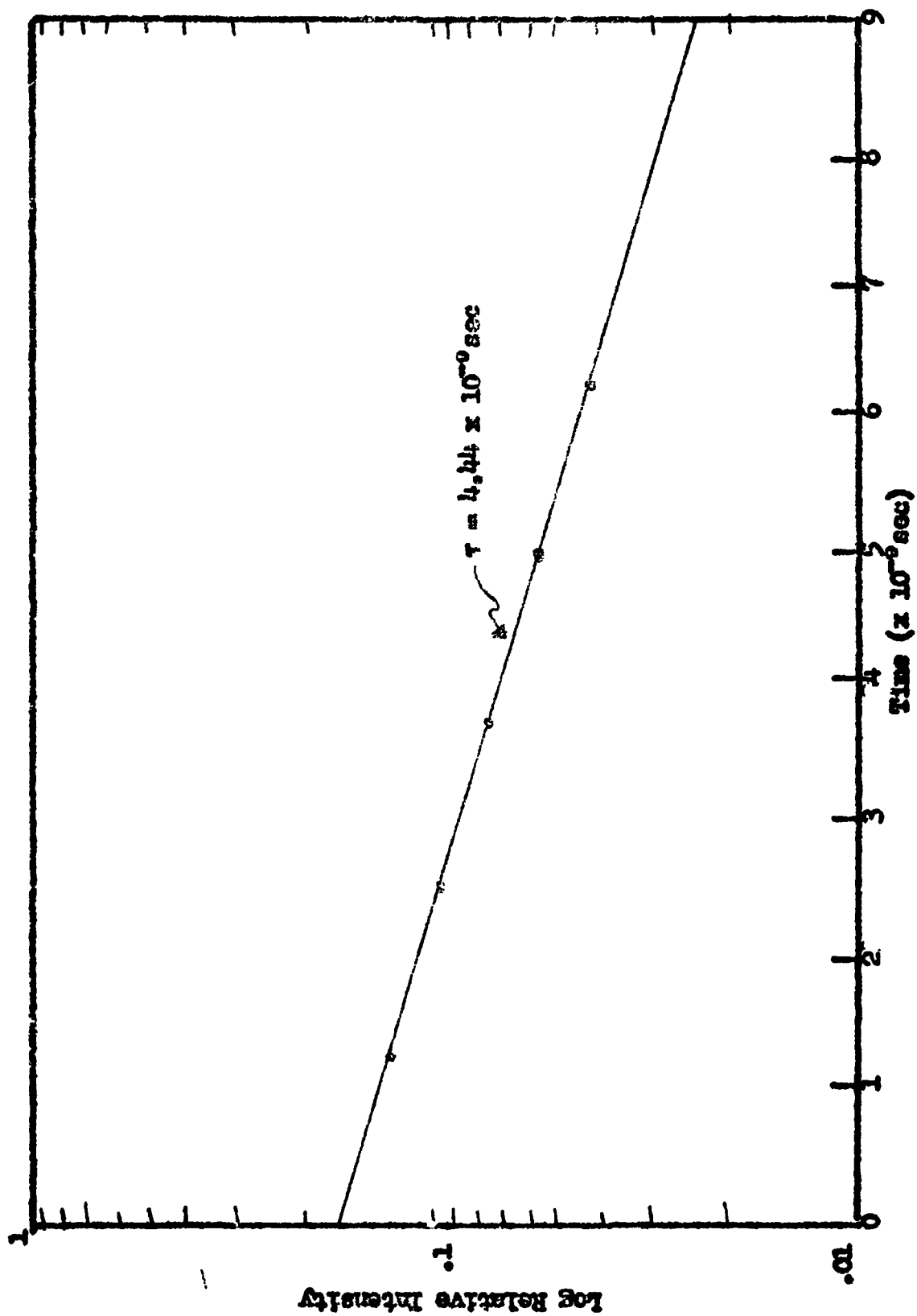
Figure 9. Intensity decay for N II, $\lambda \sim 4432\ \lambda$.

$\tau = 4.44 \times 10^{-9}$ sec
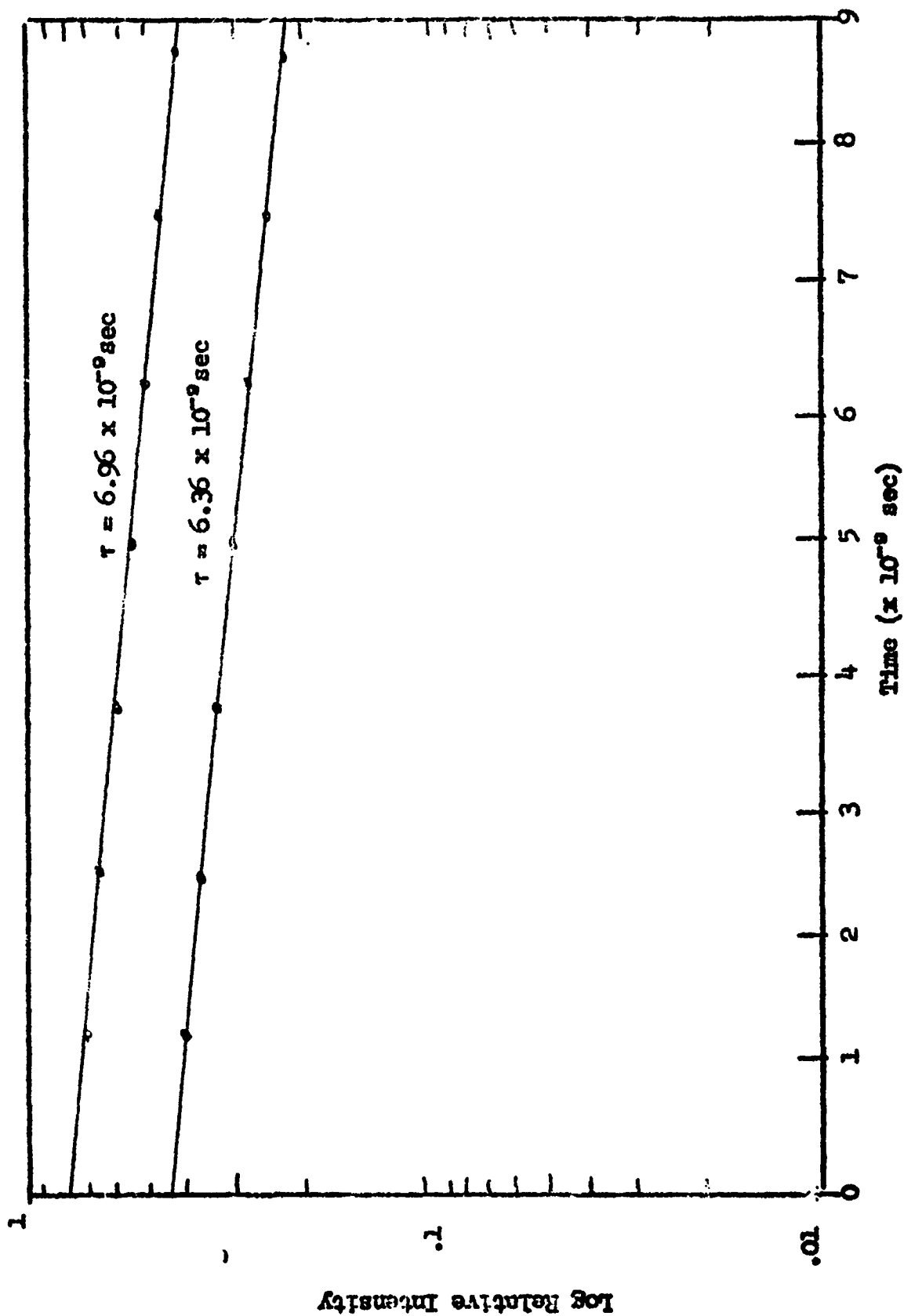
Time ($\times 10^{-9}$ sec)

Log Relative Intensity

Figure 10. Intensity decay for N II, $\lambda = 4041.3$ Å.
$2s^2 2p(^2P^o)3d^3F^o_4 - 2s^2 2p(^2P^o)4p^3G_5$
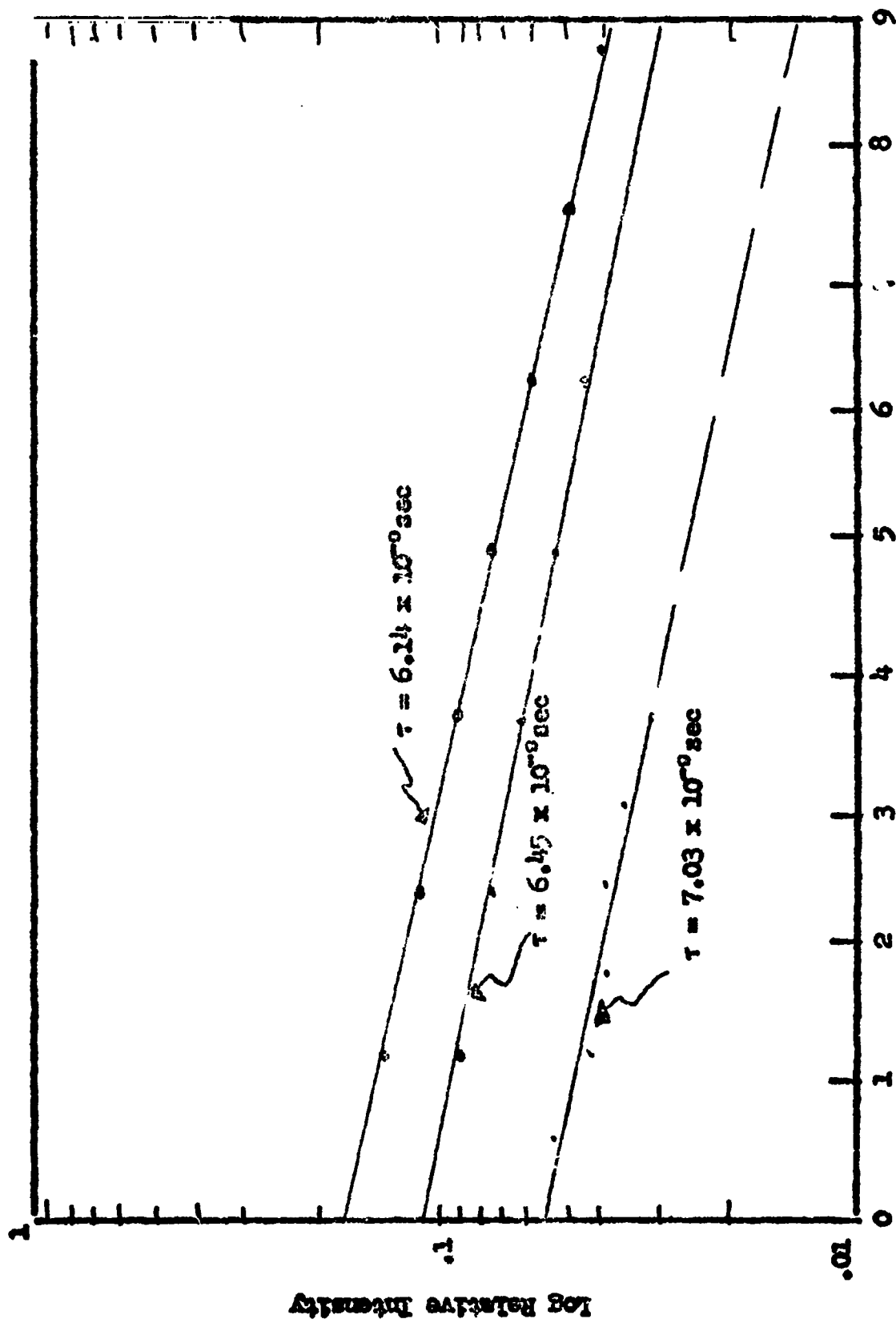
Figure 11. Intensity decay for N III, λ = 4634.2 Å.
$2s^2(^1S)3p\,^2P_{3/2} - 2s^2(^1S)3d\,^2D_{5/2}$
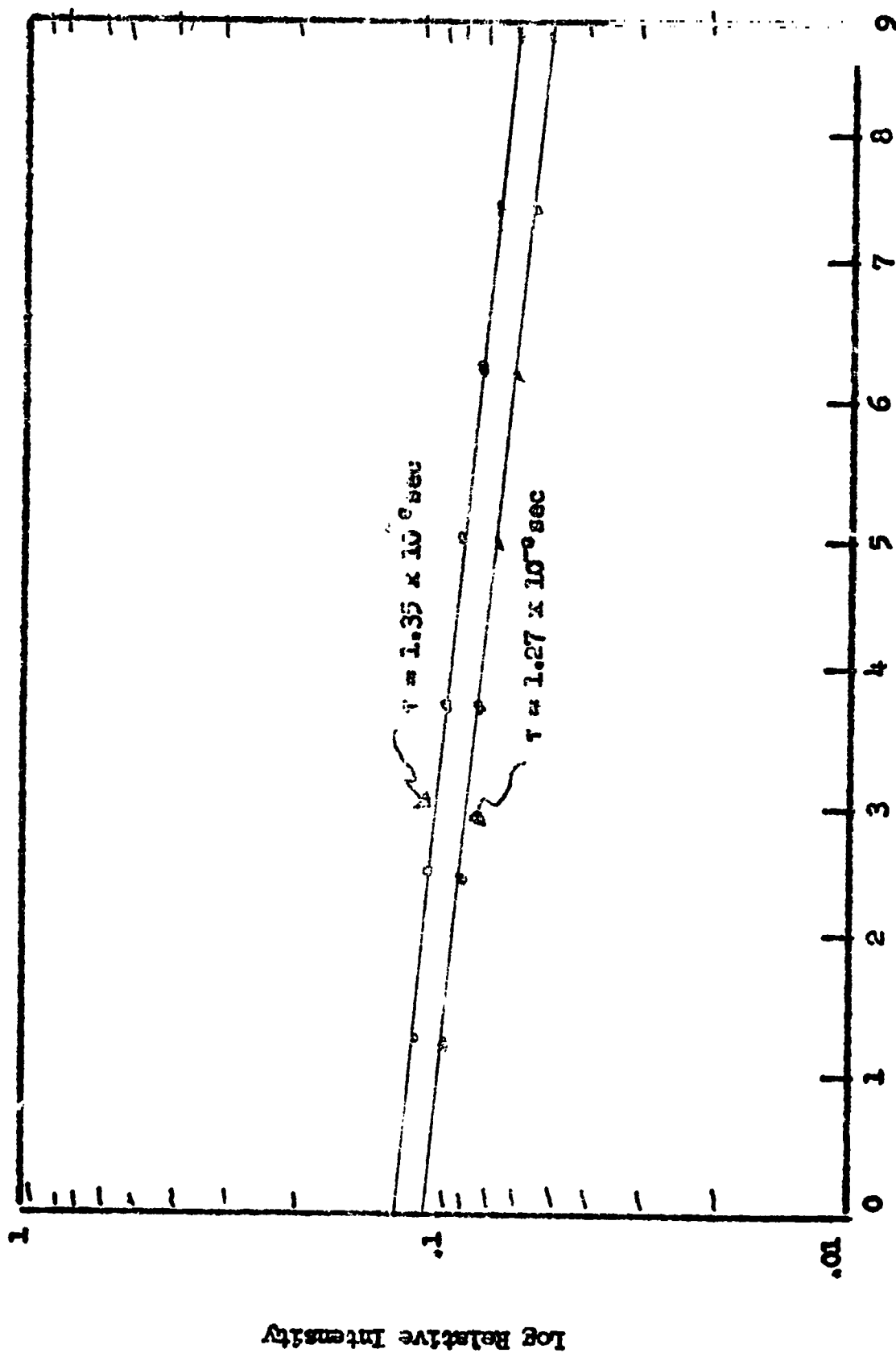
Figure 12. Intensity decay for N III, $\lambda = 4535.1$ Å.

$2s2p(^3P^o)3p\,^4D_{5/2} - 2s2p(^3P^o)3d\,^4P^o_{5/2}$

Time ($\times 10^{-9}$ sec)

Log Relative Intensity

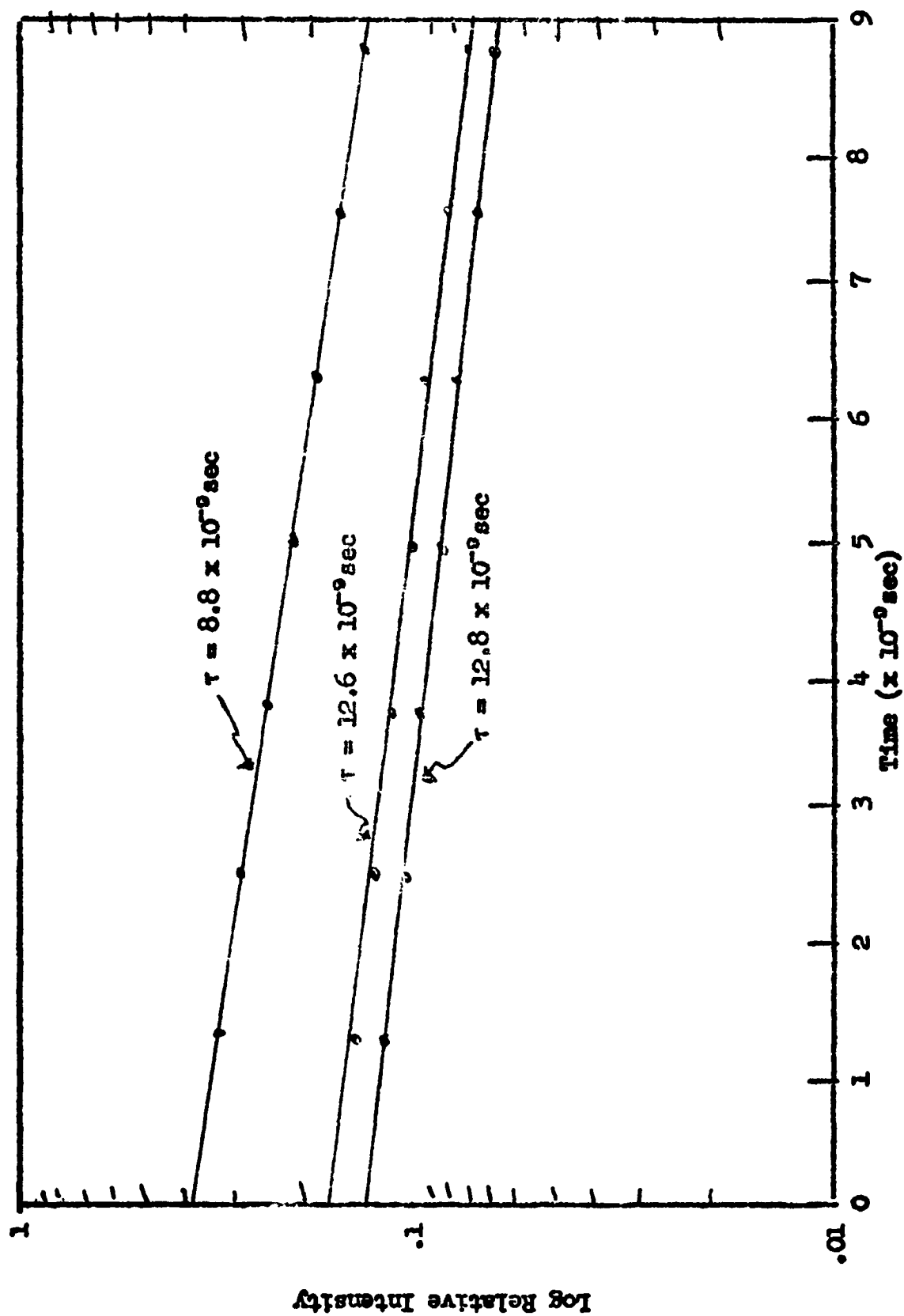$\tau = 1.35 \times 10^{-9}$ sec

$\tau = 1.27 \times 10^{-9}$ sec

Figure 13. Intensity decay for N III, λ = 4514.9 Å.
$2s2p(^3P^o)3s^4P^o_{5/2} - 2s2p(^3P^o)3p^4D_{7/2}$

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